

Electronic supplementary information (ESI)

For

**Characterization of a Rh(III) porphyrin-CO complex: its
structure and reactivity with an electron acceptor**

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1. Experimental Details

1.1. General

IR spectroscopy was recorded with FT-IR Spectrometer Frontier (Perkin Elmer). NMR spectra were obtained using JNM-ECA series (JEOL, ν (^1H) = 500 MHz). Chloroform-*d* and acetone-*d*₆ were used as a deuterated solvent for NMR analysis. These solvents contain tetramethylsilane (1%(v/v)) as an internal standard substance. The determination of CO is carried out using a gas chromatograph (Shimadzu, GC 2014) with a TCD detector. The water used in this study was purified with an Organo PURELAB Ultra Analytic and PURELITE PRB-002A unless otherwise stated.

1.2. Synthesis of $[\text{Rh}^{\text{III}}(\text{OEP})(\text{Cl})]$

2,3,7,8,12,13,17,18-Octaethylporphyrinato rhodium(III) chloride ($[\text{Rh}^{\text{III}}(\text{OEP})(\text{Cl})]$) was synthesized by the reflux of $\text{Rh}_2\text{Cl}_2(\text{CO})_4$ and 2,3,7,8,12,13,17,18-Octaethylporphyrine (OEPH_2) in toluene according to a literature [1]. Purple crystals were obtained. ESI-MS (in ethanol): m/z 635.2 ($[\text{Rh}^{\text{III}}(\text{OEP})]^+$) Anal. Calcd for $[\text{Rh}^{\text{III}}(\text{OEP})(\text{Cl})] \cdot \text{H}_2\text{O}$: C, 62.74; H, 6.73; N, 8.13. Found: C, 62.63; H, 6.66; N, 8.10. $^1\text{H-NMR}$ (CDCl_3 , 500 MHz): δ 10.34 (s, 4H), 4.24-4.06 (m, 16H), 2.00 (t, 24H, $J = 8$ Hz). $^{13}\text{C-NMR}$ (CDCl_3 , 125 MHz): δ 142.9, 140.5, 98.4, 20.1, 18.6.

1.3. Preparation and analysis of $[\text{Rh}^{\text{III}}(\text{OEP})(\text{CO})(\text{Cl})]$

[Rh^{III}(OEP)(Cl)] was dissolved in CH₂Cl₂, and the resulting solution was bubbled with CO or ¹³CO gas for 7 minutes. After bubbling, the solvent was allowed to evaporate, and the resulting crystalline powder was collected. The powder was subjected to IR analysis.

The crystalline powder of [Rh^{III}(OEP)(CO)(Cl)] was recrystallized in a mixed solvent of hexane and CH₂Cl₂ (9 : 2) to obtain good crystals that could be subjected to X-ray analysis. X-ray diffraction data were collected by a VariMax with Saturn 724+ (Rigaku) using MoK α radiation ($\lambda = 0.71075 \text{ \AA}$) at a temperature of 93 K. Based on the results of DFT calculation [2] and IR analysis, the structure was solved under the restriction that the length of C20-O1 is in the range from 1.15 \AA to 1.17 \AA .

1.4. The preparation of NQ_{red}

The reduced form of NQ (NQ_{red}) was prepared by the H₂-reduction of NQ in the presence of a Pt catalyst. NQ (4.4 μmol) was dissolved in a mixed solvent of acetone-*d*₆ (0.9 mL) and water (0.1 mL). A platinized Pt plate was immersed in this solution. The solution was purged with argon gas for 10 minutes. After then, H₂ gas was passed through the solution to reduce NQ for 10 minutes. Concomitant with evaporation of acetone, acetone-*d*₆ was replenished.

1.5. The reaction of [Rh^{III}(OEP)(CO)(Cl)] with NQ

NQ (4.4 μmol) was dissolved in a mixed solvent of acetone-*d*₆ (0.9 mL) and water

(0.1 mL) in a vial with a rubber cap. Argon gas was passed through the solution to remove dissolved oxygen. This solution was added to the crystalline powder of $[\text{Rh}^{\text{III}}(\text{OEP})(\text{CO})(\text{Cl})]$ (4.4 μmol) in a vial with a rubber cap under Ar-purge conditions, and the solution of $[\text{Rh}^{\text{III}}(\text{OEP})(\text{CO})(\text{Cl})]$ and NQ was left under argon atmosphere for 10 minutes. The product solution was subjected to NMR analysis.

1.6. The catalytic CO oxidation by NQ in the presence of $[\text{Rh}^{\text{III}}(\text{OEP})(\text{Cl})]$

NQ (10 mM) was dissolved in a mixed solvent of acetone (4.45 mL) and water (0.5 mL), and the solution was purged with argon. CO gas was passed through the solution for 7 minutes. $[\text{Rh}^{\text{III}}(\text{OEP})(\text{Cl})]$ (0.5 μmol), which was dissolved in acetone (50 μL), was injected to the NQ solution. After incubation at 25 °C for 1 hour, the gas phase was sampled and subjected to analysis with gas chromatography.

Reference

- [1] S. Yamazaki, M. Yao, N. Fujiwara, Z. Siroma, K. Yasuda, T. Ioroi, *Chem. Commun.*, 2012, **48**, 4353-4355.
- [2] Gaussian 03, Revision E.01, M.J. Frisch, et al. Gaussian, Inc. Wallingford CT (2004).

Table S1. Summary of X-ray Crystallographic of [Rh^{III}(OEP)(CO)(Cl)]

Compound	[Rh ^{III} (OEP)(CO)(Cl)]
Empirical formula	C ₃₇ H ₄₄ N ₄ O ₄ RhCl
Formula weight	699.13
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> , Å	12.620(3)
<i>b</i> , Å	8.246(2)
<i>c</i> , Å	19.435(5)
<i>β</i> , deg	100.522(4)
<i>V</i> , Å ³	1988.5(8)
<i>Z</i>	2
<i>F</i> (000)	896.00
<i>D</i> _{calc} , g/cm ³	1.451
<i>T</i> , K	93
Crystal size, mm ³	0.100 X 0.050 X 0.010
R1 [<i>I</i> >2.0σ(<i>I</i>)]	0.0798
R1 [all data]	0.0976
wR2 [<i>I</i> >2.0 (<i>I</i>)]	0.1531
wR2 [all data]	0.1616
Goodness of fit indicator	1.174

Table S2. Selected bond lengths (Å) of [Rh^{III}(OEP)(CO)(Cl)]

Rh1-C20	1.736(12)
C20-O1	1.144(16)

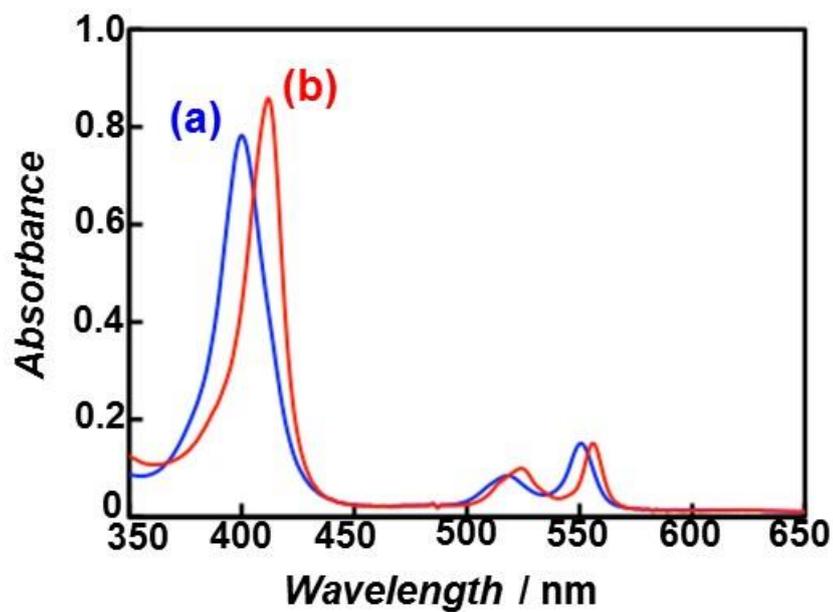


Fig. S1. UV spectra of $[\text{Rh}^{\text{III}}(\text{OEP})(\text{Cl})]$ in CH_2Cl_2 (a) before and (b) after the introduction of CO.

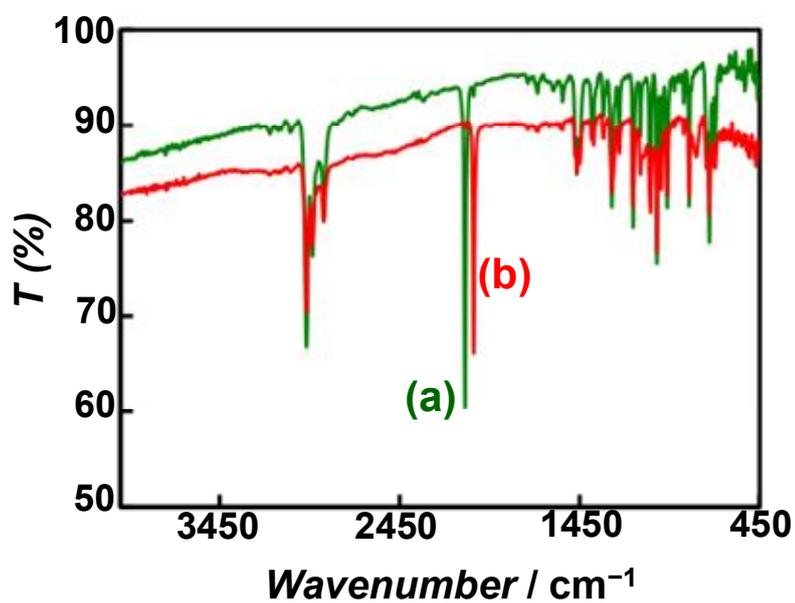


Fig. S2. IR spectra of (a) $[\text{Rh}^{\text{III}}(\text{OEP})(^{12}\text{CO})(\text{Cl})]$ and (b) $[\text{Rh}^{\text{III}}(\text{OEP})(^{13}\text{CO})(\text{Cl})]$.